
Site Charge Models for Molecular Electrostatic Potentials of Cycloalkanes and Tetrahedrane

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ABSTRACT: The molecular structures of cycloalkanes (from cyclopropane to cyclodecane) and tetrahedrane were optimized at the Hartree–Fock/6–31G** level and their molecular electric potentials (MEPs) were calculated using a geodesic grid. The MEPs were fitted using net atomic charges and several site charge models. The net atomic charge model gave very poor fits to the MEPs in every case. A model with additional methylene bisector charge sites, similar to one successfully used previously for linear alkanes, greatly improved the fits to the MEPs of these cycloalkanes. The MEPs of the highly strained molecules cyclopropane and tetrahedrane were further studied using ring center and displaced bond charge sites. The fitting of the MEP of cyclopropane was consistent with a banana bond model with asymmetrically displaced electron density in the C—C bonds. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 579–585, 1999

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Introduction

Molecules interact with each other via an intermolecular force field. One component of this force field is interaction between molecular electrostatic potentials (MEPs). Every molecule has

an MEP, which is traceable to the charged subatomic particles making up the atoms; even homoatomic molecules have a weak MEP. The importance of MEP interaction in determining the path of a reaction is well known. Short of reaction, MEPs are an important factor determining molecular docking, molecular cluster formation, and crystallization, in addition to the usual van der Waals interactions.

If MEPs of the separate molecules are known, in principle it is possible to calculate via Coulomb's

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law the intermolecular electrostatic energy for any intermolecular configuration. There are different methods of determining the MEP around a molecule. It can be directly derived from experimental X-ray electron densities studies from crystals¹ or it can be calculated from *ab initio* wave functions² because the MEP is a quantum mechanical observable quantity. Other quantum mechanical methods include semiempirical methods³ and density functional theory.⁴ In practice it is much better to have an analytical representation of the MEPs, and then the intermolecular coulombic energy between MEPs can be more quickly evaluated.

The most popular analytical representation of the MEP is the net atomic charge (AC) model⁵. Because these charges are fitted to the MEP, they are called potential-derived (PD) charges. In many cases the AC model can represent MEPs of simple organic molecules with 10% relative root mean square (RRMS) accuracy or better.⁶ Mulliken charges,⁷ also known as population analysis charges, generally give a much less accurate representation of the MEP.

The principle of the PD method is to find by least squares fitting optimum values of charge at designated sites to best fit the MEP. The charge sites are coincidentally located at nuclear sites in the AC model. The MEP is calculated at grid points located outside the nominal van der Waals radii of the atoms or some multiple of these radii. Of course, the actual charge at the nuclear site is just the nuclear charge, which is a defined physical property. What we seek is a shielded charge at the nuclear site as seen through the electron cloud surrounding the atom, which is not a defined physical property. Because we are only interested in the MEP at some distance from the atom, it is important that none of the grid points be too close to atomic nuclei; in that case the nuclei will be partially deshielded and the MEP will become more positive.

We emphasize that our basic goal is to get a relatively simple but accurate analytical representation for the MEP. Thus, the MEP model need not necessarily be chemically intuitive, such as the use of net ACs. It seems possible, however, that chemical intuition and experience might help in establishing models for the MEP that show good transferability properties between related molecules. The requirement that the MEP be well represented places a strong condition on net AC models. We found that no AC model can satisfactorily fit the

MEP of cycloalkanes, as was the case previously with *n*-alkanes.⁸

Numerous alternative methods to population analysis for determining net AC have been proposed.⁹ None of these methods seeks to directly achieve a best fit to the MEP; instead emphasis is generally placed on the chemical reasonableness and/or transferability of the charges to similar molecules. Because none of the alternative methods optimizes net AC to the MEP, a better PD model always exists that does optimize to the MEP. There is no universal definition of AC, and there are no experimentally determined charges that we can use as a criterion for the quality of the charges. In PD charges the goal is to reproduce the MEP, and the quality of a site charge model will be judged based on that definition.

There have been a number of studies on the limitations of PD charges. Some of these limitations are that they may be conformation dependent,¹⁰ influenced by the density of points,¹¹ may not be rotationally invariant,¹² depend on how and where the potential points are selected,¹³ and some of the charges might be less well determined.¹⁴ There have been numerous attempts to solve these problems. Bayly and coworkers¹⁵ suggest using a hyperbolic penalty function to restrain the fluctuation of charges of "buried" atoms. But this method results in worsening of the fit of the calculated MEP to the quantum mechanical (QM) MEP. Concerning the density of points around the van der Waals shell of the molecule, no one has come up with an ideal number of points that must be selected. While it is desirable that a very large number of points be fitted over a large van der Waals shell, there are limits imposed by computer capacity in evaluating the QM MEP. Concerning the distribution of points within the van der Waals shell, the geodesic grid suggested by Spackman¹⁶ was found to be more evenly distributed and had minimal rotational dependence compared to the Connolly or cubic grid point selection. Random selection of grid points, which are used in some PD charge calculations,¹²⁻¹⁴ makes the resulting PD charges difficult to reproduce.

There are numerous instances where the AC model failed to give a reasonably accurate representation of the MEP. Most often these failures were ascribed to the effects of lone pair electrons on the MEP. The PD site charge model could be improved by adding supplemental lone pair sites; even the location of the lone pair site could be optimized by finding the best fit to the MEP. Some

early examples of the use of lone pair sites are with the water molecule¹⁷ and azabenzenes.¹⁸ The use of additional non-AC sites was extended to a variety of organic molecules.¹⁹

Recently, it was found that the poor performance of the AC model in describing the MEP of normal (straight chain) alkanes could be dramatically improved by the addition of methylene bisector charge sites⁸ (MB model). Although the AC model works well for methane, it fails badly for the higher alkanes. For instance, the RRMS error of fit to the AC model for ethane was found to be 97%. With the addition of MB sites the fit improved to only 7% RRMS error. In addition, negative charges for hydrogen atoms were indicated by the AC model, which is considered contrary to normally assigned electronegativities for carbon and hydrogen atoms in organic molecules. When MB sites are included, hydrogen atoms are always more positive than carbon.

The optimum distance of the MB site from carbon in normal alkanes was found to be approximately 0.6 Å. The charge on the MB sites of all of the normal alkanes up to decane was almost always negative, suggesting an accumulation of electron density between hydrogen atoms of the CH₂ group. An experimental electron density study of ethane by X-ray diffraction indeed showed a buildup of charge at the MB sites.²⁰

A charge accumulation between nonbonded hydrogens was also found in theoretical electron density studies of the water molecule.²¹ This charge was located on the twofold axis along a line bisecting the H—O—H angle between the hydrogens. A later refinement of this model using a PD model led to placement of a pair of out of plane negatively charged sites above and below the H—O—H plane but still more or less between the hydrogens. This model is referred to as the reverse lone pair PD model for water.¹⁷

STRUCTURE OPTIMIZATION

Eight cycloalkanes from cyclopropane to cyclodecane were examined in this study. In addition, the structure of tetrahedrane was considered. Each molecular structure was quantum mechanically optimized using Gaussian 94²² at the Hartree-Fock (HF)/6-31G** level. Starting models for optimization were taken from the crystal structures of C₃—C₇ and C₁₀ rings; C₈ and C₉ rings and tetrahedrane were optimized starting from the coordinates obtained from molecular mechanics energy minimizations. The characteriza-

TABLE I. _____
Characterization of Starting Structures.

Molecule	Conformation
Cyclopropane	Planar ²³
Cyclobutane	Puckered in gas phase and planar in crystal ²⁴
Cyclopentane	"Envelope" ²⁵
Cyclohexane	Chair ²⁶
Cycloheptane	Twist-chair ^{27,28}
Cyclooctane	Chair-boat ²⁸⁻³⁰
Cyclononane	Twist-boat-chair ^{28,29}
Cyclodecane	Boat-chair-boat ^{28,29}
Tetrahedrane	Tetrahedral

tions of the starting structures are given in Table I. In contrast to straight chain alkanes, cycloalkanes are more or less strained because of the ring closure. This strain is illustrated by changes of C—C—C angles and C—C—C—C torsions in cycloalkanes from normal straight chain values of 112 and 180°, respectively. The tetrahedrane molecule is also highly strained, having four cyclopropane type faces. Figure 1 shows the optimized structures.

CALCULATION AND FITTING OF MEP

The MEP of each molecule with its structure optimized as described above was calculated at the HF/6-31G** level on a layered fourfold tessellated icosahedral geodesic grid constructed around each molecule.¹⁶ The first layer was positioned at 1.6 times the van der Waals radius of the atom. Hydrogen was assigned a van der Waals radius of 1.2 Å and carbon 1.7 Å. The next four successive layers were positioned at 1.8, 2.0, 2.2, and 2.4 times the van der Waals radius. Depending on the size of the ring, the number of points varied from 1276 points for cyclopropane to 2388 points for cyclodecane. Optimum least squares fits to the MEPs were found using the AC and MB models with the pdm97³¹ computer program. The extra MB sites were located along the MBs at 0.6 Å from the carbon. Table II shows the RRMS fits obtained with these models and with Mulliken charges.

COMPARISON OF SITE CHARGE MODELS

Mulliken charges generally give very poor fits to the MEPs of cycloalkanes with up to 228% RRMS error; they will not be further discussed. In the case of Mulliken charges errors can exceed

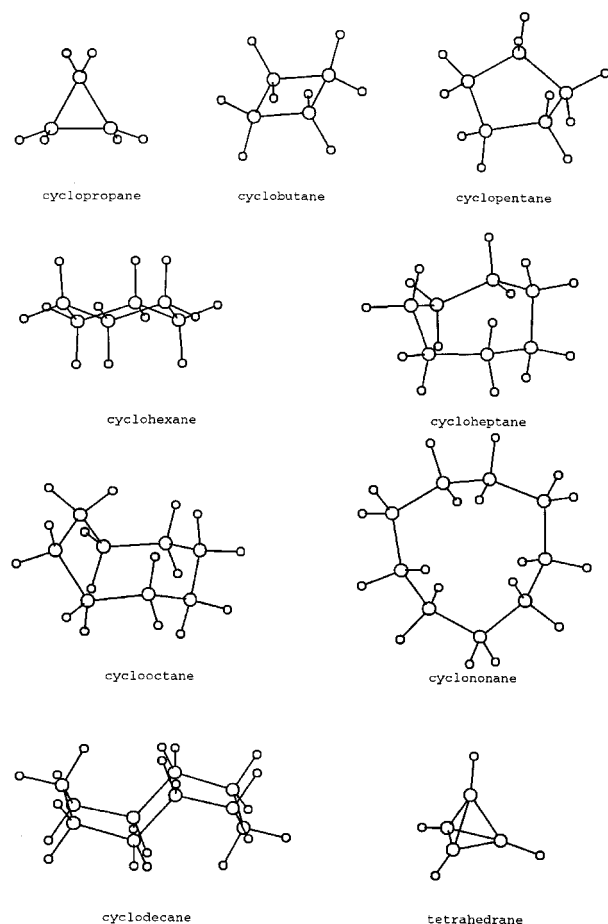


FIGURE 1. Molecular structures of cyclopropane to cyclodecane and of tetrahedrane.

100% because these charges are not directly optimized or scaled to the MEP. There have been numerous efforts to revise Mulliken-type charges, often with an aim to improve their chemical reasonableness. None of these alternative definitions

of net AC corresponds to a physical quantity defined by a QM operator on the wave function. In our view the important thing to do is to get a good representation of the MEP around the molecule, regardless of the chemical reasonableness of the model. Of course, if the MEP model makes some sense in chemical terms, so much the better.

The quality of MEP fit can be expressed by the RMS error (in kilojoules/mole) or the RRMS error (in percent). The RRMS errors of fit for PD charges are always equal or less than 100% because these charges are optimized to the MEPs. For AC model charges the RRMS errors for the cycloalkanes range from 52.6 to 99.4%; the AC model for the MEP of these hydrocarbons was also poor. Table III shows values for the PD charges.

The use of the additional sites of the MB model leads to substantial improvement over the AC model; the RRMS fits then range from 12.7 to 16.8%. In contrast to the AC model, hydrogen atoms are almost always more positively charged than carbon atoms and hydrogen is always positively charged. As with straight chain alkanes, MB sites are always negative, consistent with the idea that there is a buildup of electron density between hydrogens of a methylene group. The values of the MB site charge ranged from -0.154 to -0.121 ; this remarkable uniformity of MB site charge values lends credence to this model and augurs well for charge transferability to larger molecules.

To compensate for negative MB site charges, generally carbon and hydrogen atoms become more positive compared to AC model charges. Sometimes AC model charges for H are negative; this is contradictory to normally assigned electronegativity values for carbon and hydrogen. In the AC model H charges range from -0.048 to

TABLE II.
RMS (kJ/mol) and RRMS fit (%) of Site Charge Models.

Molecule	Mulliken		AC		MB	
	RMS	RRMS	RMS	RRMS	RMS	RRMS
Cyclopropane	5.22	56.4	4.65	52.6	1.33, 0.66 ^a	15.9, 7.9 ^a
Cyclobutane	5.31	138.4	3.82	99.4	0.64, 0.94 ^a	16.8, 24.5 ^a
Cyclopentane	6.22	187.1	3.08	92.8	0.58	17.5
Cyclohexane	6.26	226.0	2.41	87.1	0.35	12.7
Cycloheptane	6.48	228.3	2.51	88.5	0.42	15.0
Cyclooctane	6.16	208.1	2.53	85.5	0.44	15.0
Cyclononane	5.02	160.7	2.37	75.7	0.47	15.0
Cyclodecane	5.70	200.1	2.31	81.1	0.46	16.3
Tetrahedrane	2.60	23.3	1.99	17.8	0.34 ^a	3.10 ^a

^a RC model with no MB site.

TABLE III.
Comparison of Charges for AC and MB Models ($|e|$).

	Site	AC	MB
Cyclopropane	C	−0.342 (3)	−0.242 (3)
	H	0.171 (6)	0.196 (6)
	MB site		−0.150 (3)
Cyclobutane	C	−0.024 (4)	−0.062 (4)
	H	0.012 (8)	0.092 (8)
	MB site		−0.121 (4)
Cyclopentane	C	0.002 (2), 0.002 (2)	−0.058 (2), −0.072 (2)
		−0.003 (1)	−0.029 (1)
	H	−0.009 (4), 0.008 (4)	0.090 (4), 0.094 (4)
		0.000 (2)	0.082 (2)
	MB site		−0.121 (2), −0.124 (2)
Cyclohexane	C	−0.026 (6)	−0.059 (6)
	H	0.021 (6) [ax], 0.005 (6) [eq]	0.095 (6) [ax], 0.103 (6) [eq]
	MB site		−0.139 (6)
Cycloheptane	C	−0.042 (2), −0.038 (2)	−0.058 (2), −0.030 (2)
		−0.048 (2), −0.032 (1)	−0.070 (2), −0.009 (1)
	H	0.013 (4), 0.026 (4)	0.097 (4), 0.089 (2)
		0.036 (2), 0.015 (4)	0.098 (2), 0.087 (2)
	MB sites		0.091 (2), 0.078 (2)
			−0.154 (2), −0.128 (1)
Cyclooctane	C	−0.124 (4), 0.014 (2)	−0.134 (2), −0.124 (2)
		−0.022 (2)	−0.012 (4), −0.051 (2)
	H	0.063 (2), 0.039 (4)	−0.076 (2)
		0.016 (6), 0.033 (2)	0.086 (2), 0.089 (4)
	MB sites	0.034 (2)	0.091 (6), 0.087 (2)
			0.081 (2)
Cyclononane	C	−0.078 (6), −0.125 (3)	−0.154 (2), −0.142 (2)
			−0.141 (2), −0.117 (2)
	H	0.043 (12), 0.055 (6)	−0.062 (4), −0.014 (3)
	MB sites		−0.061 (2)
Cyclodecane	C	0.087 (2), −0.001 (4)	0.095 (12), 0.099 (6)
		−0.260 (4)	−0.141 (2), −0.160 (3)
	H	0.047 (4), 0.022 (4)	−0.140 (4)
		0.076 (4), 0.063 (4)	−0.094 (2), −0.085 (4)
	MB sites	0.018 (2), −0.048 (2)	−0.010 (4)
			0.102 (4), 0.094 (4)

The numbers in parentheses are the multiplicities. The MB distance is 0.6 Å from the carbon.

0.171; in the MB model hydrogen charges range from 0.078 to 0.196. In the AC model C charges range from −0.342 to 0.087; in the MB model C charges range from −0.242 to −0.009. Note that in the MB model not only have the carbon and hydrogen charges become generally more positive, but also their ranges have been reduced such that carbon never has net positive charge.

Several additional site charge models were evaluated for the highly strained rings of cyclopropane and tetrahydronaphthalene. In these highly strained small molecules there are strong carbon–carbon interactions across the three-membered rings, and therefore it is possible that use of a ring center (RC) charge site would improve fit to the MEP. Table II shows that the RC model (with no MB sites) for

cyclopropane is indeed better than the MB model, giving a RRMS fit of 7.9%. Note, however, that the RC model for cyclobutane is inferior to the MB model; the RRMS fit increases from 16.8% for the MB model to 24.5% for the RC model. This success of the MB model relative to the RC model is consistent with the considerably reduced strain in cyclobutane, making its MB sites more like those of the normal alkanes.

The RC model was also evaluated for tetrahydrene; because this molecule does not have CH₂ groups, the MB model is irrelevant. The AC model for tetrahydrene gave a RRMS fit of 17.8%, but this fit could be dramatically improved to 3.1% by addition of the four RC sites of the RC model. Thus, the successful RC site charge model for cyclopropane may also be extended to tetrahydrene.

Table IV shows a comparison of charges for AC and RC models for the MEPs of cyclopropane and tetrahydrene. The RC sites have large positive values; to maintain neutrality the carbon sites become more negative. Hydrogen sites keep about the same positive charge in cyclopropane, but in tetrahydrene they become more positive.

COMPARISON WITH EXPERIMENTAL ELECTRON DENSITY STUDIES

Experimental electron studies can be used to detect the possible buildup of electron density in bonds.³² Normally this electron density buildup occurs along the bond axis. But theory suggests, and experiment confirms, that bonding electron density is shifted outward of the C—C axis in small rings, especially cyclopropane rings. This has been called the “banana bond” effect. In addition, there is the possibility of electron density changes at the centers of small rings. It is of interest to study banana bond and ring charge effects using PD models for the MEP.

TABLE IV. AC and RC Model Charges for Cyclopropane and Tetrahydrene.

	Site	AC	RC
Cyclopropane	C	−0.342	−0.652
	H	0.171	0.172
	RC		0.927
Tetrahydrene	C	−0.193	−1.731
	H	0.193	0.342
	RC		1.388

Nijveldt and Vos²³ investigated the different electron densities in cyclopropane and two substituted cyclopropanes by X-ray diffraction. They found difference electron density peaks at positions expected for buildup of electron density in banana bonds. From their figure 8 the outward displacement of the electron density is shown as approximately 0.15 Å. We will call this outward displacement the bond asymmetry parameter X. The ring center of cyclopropane also shows some electron density buildup, but less than that of the bonds.

We investigated the use of linear and asymmetric bond charge BC(X) sites in cyclopropane to improve the fit to the MEP. The starting model for cyclopropane was the AC + RC model discussed above, which gave an RRMS fit of 7.9%; Table V shows RRMS fit values to the MEP for AC + RC + BC(X) models. The addition of BC sites improves the MEP fit to 7.0%; for cyclopropane the fit is flat as X goes from zero to 0.2 Å, then it slightly increases. The corresponding optimized BC is largest when X = 0.0 and it decreases in magnitude to −0.184 when X = 0.2. Thus, although the MEP fit does not improve as X increases, the BC model is consistent with a possible bond displacement of up to 0.2 Å.

TABLE V. RMS (kJ/mol) and RRMS (%) Fit and BC(X) Charges of Cyclopropane and Tetrahydrene.

Cyclopropane			
X	AC + RC + BC(X) Fit		BC(X) Charges
	RMS	RRMS	
0.0	0.58	7.0	−0.461
0.1	0.58	7.0	−0.281
0.2	0.58	7.0	−0.184
0.3	0.59	7.1	−0.126
0.4	0.60	7.2	−0.089
0.5	0.60	7.3	−0.064
Tetrahydrene			
0.0	0.17	1.5	−0.890
0.1	0.31	3.0	−0.004
0.2	0.31	3.0	−0.002
0.3	0.31	3.0	−0.001
0.4	0.31	3.0	−0.001
0.5	0.31	3.0	−0.001

To further study the BC displacement phenomenon using the MEP, we applied the AC + RC + BC(*X*) model to tetrahedrane, where *X* is measured out along the edge bisector. The results are shown in Table V. The RRMS fit to the tetrahedrane MEP is quite good (3% or better) for values of *X* up to at least 0.5 Å. There does seem to be a preference for *X* = 0.0 where the fit further improves to 1.5%. The fitting to the tetrahedrane MEP is best using a very small bond asymmetry parameter, but if a 3% fitting criterion is used larger *X* values are allowed. Experimental X-ray electron density studies³³ for *tetra*(*t*-butyl)tetrahedrane show that the tetrahedrane moiety in this molecule has banana bonds with an apparent BC displacement of about 0.3 Å. The effects of the four *t*-butyl group substituents on banana bonding is not known as compared to the parent tetrahedrane molecule.

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